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INTERACTION OF COPPER WITH A VAPOR DEPOSITED POLYIMIDE FILM

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ABSTRACT

The interaction of copper with a vapor deposited film of PMDA-ODA polyimide was studied using x-ray photoelectron spectroscopy (XPS) and scanning tunnelling microscopy (STM). Copper was evaporated onto the polyimide surface to a total thickness estimated to be about five atomic layers. The copper initially interacts with the planar imide ring - the nitrogen XPS signal is preferentially attenuated, some copper is oxidized, and the carbonyl XPS intensities are altered. We find no evidence for chemical interaction with the ODA part of the polyimide. Heating the copper covered surface leads to redistribution of copper, probably below the surface as reported in earlier studies. STM images of the heated surfaces show that substantial surface roughening has occurred.

I. Introduction.

Good interfacial adhesion is important for the application of polyimides in microelectronic packaging [1-3]. In this paper we describe the initial stages in the interaction of copper with a vapor deposited PMDA-ODA polyimide film as observed with x-ray photoelectron spectroscopy (XPS) and scanning tunnelling microscopy (STM).

In previous studies of the interaction of copper with PMDA-ODA polyimide films, the films were prepared by spin coating a thin layer of a solution containing polyamic acid followed by thermal curing [4-8]. Copper is reported to interact weakly with the ether oxygen in the ODA part of the polyimide [6-8]. Some of the copper penetrates into the polyimide where it forms metallic precipitates even at room temperature [8]. Heating also causes copper to aggregate into clumps on the surface [5,8].

In the present study, the polyimide film was formed by a vapor deposition technique [9,10]. PMDA (1,2,4,5-benzenetetracarboxylic anhydride) and ODA (1,4-oxydianiline) are simultaneously deposited onto a substrate where they react to form the intermediate polyamic acid. This layer is then cured to form the PMDA-ODA polyimide. The vapor deposited material is identical to the spin coated material as characterized by XPS although it may have substantially lower molecular weight [10]. We find that the interaction of copper with vapor deposited films is stronger than reported for spin-coated films. In particular, our results indicate that copper initially forms a complex with the imide portion of the polymer and possibly breaks some imide linkages. Some of the copper also diffuses into the vapor deposited films and the surface roughens.

II. Experimental Techniques.

The samples used in these experiments were prepared and initially characterized in an ultra-high vacuum (UHV) chamber equipped for x-ray photoelectron spectroscopy (XPS). The

XPS system was built by Vacuum Science Workshop and consists of a dual anode (Mg or Al) x-ray source and an HA 5000 hemispherical electrostatic analyzer. All data presented in this report were obtained in the constant pass energy mode with 25 eV pass energy. The energy resolution in this mode is about 1.6 eV. PMDA-ODA films in the thickness range used in this study are charged during an XPS measurement [10,11]. The amount of charging is not reproducible from film to film but typically caused charging shifts of the XPS to higher binding energies of up to about 5 eV. The data presented in this paper is not corrected for the charging shifts; the spectra in Figs. 2 and 4 have a charging shift of about 4 eV and that in Fig.3 has a shift of about 0.8 eV.

A Digital Instruments Nanoscope I scanning tunnelling microscope (STM) was used to characterize the surface morphology. This instrument operates in air so that the samples had to be removed from the vacuum chamber and consequently exposed to air prior to imaging. Tips were Pt80Ir20 alloy. Images were recorded in the constant current (2.0 nA, 25 mV) mode with tunneling from the tip to the sample and were photographed from the screen of a storage oscilloscope.

The PMDA-ODA films were supported on Ni(110) and Cu(111) single crystals. There were no observable differences between the PMDA-ODA films formed on these two substrates. The surface morphology of the Ni(110) substrate was characterized by STM prior to formation of the polymer film. The sample was cleaned by argon ion sputtering, followed by annealing for about one hour in ultra-high vacuum. It was then cooled to room temperature, removed from the vacuum chamber and rapidly transported to the STM. Three typical images, all obtained from different 100 nm by 90 nm areas within one-half hour of removal from the vacuum chamber, are shown in Fig 1(a)-(c). Although the surfaces are not completely flat, each image clearly shows that there are large flat regions. It should be kept in mind that the sample used for Fig 1 had been transported through air and therefore was coated with a layer of oxide and probably contaminated with

other adsorbed gases, including water molecules. Prior to coating with a PMDA-ODA film, the metal substrates were cleaned by cycles of argon ion bombardment and annealing.

The PMDA-ODA films used in this study were prepared by in situ vapor deposition of PMDA and ODA molecules from separate sources as described previously [10]. At the start of a deposition, the sources are translated into the main vacuum chamber and positioned directly in front of the substrate. Upon completion of the deposition, typically 10 to 20 min, the sources are withdrawn into a separately pumped side chamber and a gate valve closed. The deposited layer is heated to 250 - 300 °C to drive off excess ODA and cure the polyimide.

The resulting film is characterized by XPS to check that imidization is complete and that the film is thick enough to attenuate the Ni or Cu 2p_{3/2} emission by more than 99 percent. Based on our previous studies, the resulting PMDA-ODA films are about 10 nm thick, continuous and conform to the substrate morphology [10,11]. The upper spectrum in each panel of Fig. 2 (not corrected for a 4 eV charging shift) is from a film prepared in this way and agrees with previous studies [6-11]. The O 1s peak, Fig. 2a, is an unresolved doublet with a shake-up feature at about 6 eV higher binding energy. The low binding energy component of the doublet is due to the carbonyl oxygens on the PMDA portion of the polymer and the high binding energy component is due to the ether oxygen on the ODA component. The N 1s line, Fig. 2b, consists of a single peak at 404.4 eV between two Cu Auger features at 399 eV and 411 eV. The absence of a shoulder on the low binding energy side of the N 1s line is indicative of a high quality film. The C 1s emission is shown in Fig. 2c. The carbonyl carbon signal is at 292.5 eV.

Our previous studies of PMDA-ODA coated surfaces of Au and Cu showed that STM images of the polyimide coated surfaces are indistinguishable from images of the substrate except for isolated small regions in which molecular order occurs [11]. Based on this experience, STM images of the coated Cu substrates prior to Cu deposition were not obtained in the present study.

Cu was deposited from an evaporation source consisting of a W wire basket heated by direct current. A deposition monitor was not available to calibrate the deposition rates but, based on attenuation of the XPS signals from the underlying PMDA-ODA film, the deposition rates were estimated to be approximately 0.7 nm/hr. The substrate was kept at room temperature (about 300 K) during deposition.

III. Results.

A. Deposition at Room Temperature.

Copper was deposited onto the fully cured PMDA-ODA film which was at about 300 K. Figure 3a shows the increase of the Cu $2p_{3/2}$ integrated intensity following dosing times of 6, 12, 24, 48, and 96 min. Following the 6 min dose, the sample was allowed to sit overnight. During this time the Cu $2p_{3/2}$ signal decreased by about 15 percent without change in lineshape, the N 1s intensity remained constant, and the C 1s and O 1s intensities decreased by about 5 percent. These changes indicate a change in the distribution of Cu in the near surface region due to diffusion into the PMDA-ODA substrate and/or to formation of Cu aggregates on the surface.

Cu deposition did not change the XPS charging shifts of the clean PMDA-ODA films. Therefore, we conclude that regardless of the details of the Cu interaction, the static dielectric character of the PMDA-ODA films is preserved. This contrasts with films of PMDA-ODA formed on Cu substrates by spin coating methods [12] where the solvent plays an important role [13,14] in altering the dielectric character of the film.

For doses of 2 min and 12 min, the Cu $2p_{3/2}$ lineshape is broader than for all higher doses as shown by comparison with the shape after 96 min deposition in the insert in Fig 3a. If the Cu were in a metallic state, the Cu $2p_{3/2}$ lineshape would be determined by the spectrometer resolution. Furthermore, there is no shake-up feature near 940 eV as

would be expected if Cu was in the fully oxidized 2⁺-state. Therefore, we conclude that at least some of the initial Cu deposit appears to be in the partially oxidized 1⁺-state. This interpretation is also consistent with changes in the O 1s emission discussed below.

Additional insight into the Cu interaction is gained from changes in the XPS emission from the PMDA-ODA substrate. If the Cu layer is uniform, the substrate attenuation is [10]

$$I = I_0 e^{-t/\lambda}$$

where I_0 is the intensity from the clean PMDA-ODA surface, t is the thickness of the Cu layer and λ is the electron mean-free pathlength in Cu. Figure 3b shows the attenuation of the C 1s, N 1s, and O 1s integrated intensities as a function of deposition time. The C and O are attenuated at about the same rate while the N signal is more strongly reduced. If the O 1s, N 1s, and C 1s photoelectron mean-free pathlengths are assumed to be approximately 1.0 nm in copper [10,15], the 24 min deposition corresponds to one monolayer (one monolayer equals 7×10^{15} copper atoms/cm²) and the total deposition of 96 min to about 5 monolayers.

Changes in the O 1s, N 1s and C 1s emission during Cu deposition are illustrated in Figs 2a - 2c, respectively. The N 1s signal decreases in maximum intensity without change in lineshape. Thus, no new chemical states of N are created at the surface by Cu deposition. The O 1s intensity also decreases and a new component is formed with binding energy of 535 eV (not corrected for a 4 eV charging shift); this binding energy is characteristic of metal oxides and is thus consistent with formation of some oxidized Cu at the interface. The major change in the C 1s emission is a slight reduction and broadening of the carbonyl carbon intensity at about 292 eV. The broadening suggests that these changes cannot be due to attenuation by the Cu overlayer. These observations are consistent with Cu interaction with PMDA-ODA via its planar imide ring causing some

carbonyl to reduced to form an oxide. Some N atoms may be removed or are preferentially attenuated by the overlying Cu layer.

B Effects of Annealing.

Following the 96 min total dose of Cu, the sample was heated for 30 min at 375 K, 425 K, 475 K, 525 K and 575 K. An additional heating for 90 min at 575K caused no further change. After each annealing cycle, the sample was cooled to room temperature and a set of XPS spectra obtained. The decrease of the Cu 2p_{3/2} signal, Fig 4, could be due to diffusion of Cu into the substrate, to conglomeration of Cu into small particles at the surface, or to a combination of the two. The insert in Fig 4b compares the 300 K and 575 K data and shows that heating does not change the Cu 2p_{3/2} lineshape.

Figure 2a shows the effect of heating on the O 1s emission. The oxidic oxygen component at 535 eV disappears and the integrated O 1s intensity decreases. Thus, the oxidic oxygen must be leaving the surface region. Direct comparison with the clean PMDA-ODA O 1s lineshape shows that there is also a slight decrease in the low binding energy carbonyl portion of the O 1s intensity at about 536 eV, but essentially no change in the ether component. This observation suggests that Cu does not interacted significantly with the ether O.

Following heating, the intensity of the low binding energy component of the C 1s emission has increased slightly while the carbonyl peak has decreased by a small amount. This is shown in Fig 2c. The increase in non-carbonyl signal indicates that Cu may be leaving those portions of the surface and accumulating near the carbonyl groups.

Neither the intensity nor the shape of the N 1s emission changes during the heating as illustrated in Fig 2b. This lack of change indicates that the chemical environment of the imide N does not significantly change during annealing. In particular, no new N chemical states form and the amount of Cu over the imide linkage does not change. This latter

observation indicates that any Cu complex that involves the imide linkage must be stable under these temperature conditions.

Taken together, the XPS results suggest that some Cu may accumulate near the carbonyl groups on the surface during heating but that this occurs without increasing the coverage over the N. At the same time, Cu coverage of other portions of the PMDA-ODA unit actually decreases. Thus, magnitude of the overall decrease in Cu intensity can not be accounted for by conglomeration of copper into particles that are smaller than the polyimide structural unit. Thus, it seems most likely to us that most of the Cu is diffusing below the surface as is also reported for Cu on the surface of spin-coated PMDA-ODA films [5,8].

STM images were obtained from both the Ni(110) and Cu(111) substrates following the final heat treatment at 575 K. Similar results were obtained in both cases. The samples were removed from the UHV chamber and transported through air to the STM. Figures 1d-1f show three images taken from the Ni(110) sample. These images are qualitatively different from the "clean" surface images shown in Fig 1a-1c. In particular, the surface is substantially rougher. Surface protrusions have lateral dimensions of 10 - 20 nm and heights as large as 5 - 6 nm. These heights are about one-half the initial polyimide film thickness. In order to be consistent with the XPS data, these protrusions must be caused by Cu penetration below the surface possibly to form small particles [5,8]. We note also that these ex situ STM measurements might be influenced by the uptake of water. The copper-polyimide composite does remain thick enough to completely attenuate the Ni XPS signals from the substrate and the charging shift is not changed by either the deposition or the subsequent heating.

IV. Conclusions.

We have studied the interaction of copper overlayers with PMDA-ODA films formed by vapor deposition. Our results suggest that the interaction is slightly stronger than reported

in previous studies of spin coated films. The copper films were deposited at 300 K up to a thickness of about five monolayers. The formation of oxidized copper during the initial deposition indicates some chemical attack of the carbonyl groups as also reported by Dunn and Grant for 10 Å films of copper [4]. The simultaneous enhanced reduction of the N 1s XPS signal shows that copper either preferentially accumulates on the planar imide rings or that some nitrogen is actually removed from the surface region as a consequence of the chemical interaction of copper with the polyimide film. A similar enhanced reduction in N 1s intensity occurs during the first 5 Å of Al deposition on PMDA-ODA films and has been interpreted as evidence for formation of a metal-carbonyl complex [16]. The report by Dunn and Grant [4] of no change in the imide related modes in infra-red absorption is consistent with rupture of the polyimide caused by removal of nitrogen atoms.

We find no evidence for significant chemical interaction of copper with the ODA portion of the polyimide. This contrasts with previous studies [6].

STM measurements carried out in air, show that the surface of the annealed films are much rougher than the underlying substrate. Similar results have also been found for Ti overlayers [17]. Future STM measurements need to be done in ultra-high vacuum in a spectroscopy mode. This will eliminate any artifacts, such as uptake of water, caused by exposure of the samples to air and may also allow us to determine whether copper completely covers the surface.

Neither copper deposition nor heating changes the magnitude of the XPS charging shift. This indicates that the static dielectric properties of the PMDA-ODA film are not significantly altered by interaction with copper. This contrasts with the behavior observed for interfaces formed by spin-coating polyimide onto copper substrates where interactions between copper and both the solvent and polyamic acid lead to changes in the electrical properties of the polyimide [12].

Acknowledgements.

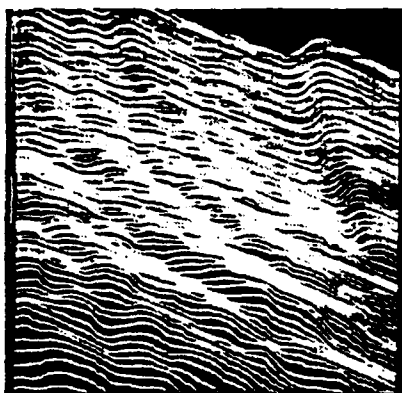
This research was supported by IBM, Endicott, NY. Fabrication of the PMDA-ODA substrates was supported by the Office of Naval Research.

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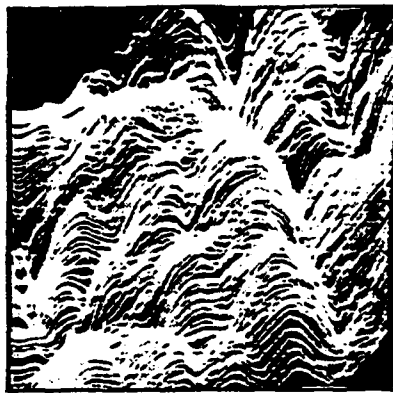
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Figure Captions

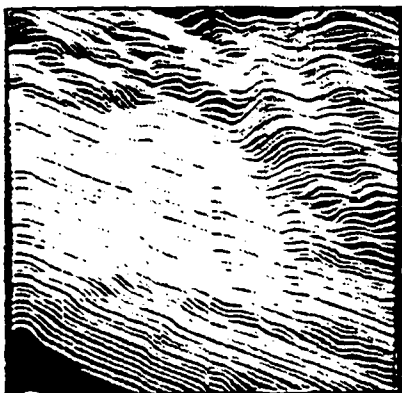
- Figure One.** Scanning tunneling microscope images of (a)-(c) the clean, air-exposed Ni(110) surface and (d)-(f) the copper coated polyimide film following annealing to 575 K. The images are from 100 nm x 90 nm regions and the length of the vertical bar in the center of the figure corresponds to 4 nm vertical distance.
- Figure Two.** Comparison of the XPS signals from the clean PMDA-ODA surface, after 96 min deposition of Cu, and after heating to 575 K for 90 min. (a) O 1s; (b) N 1s; (c) C 1s. The binding energy scale has not been corrected for a 4 eV charging shift. The PMDA-ODA film was grown on a Ni(110) substrate.
- Figure Three.** (a) Changes in the Cu 2p_{3/2} intensity vs deposition time onto a PMDA-ODA film at 300 K. The PMDA-ODA film was grown on a Cu(111) substrate. The insert compares the lineshape for low and high coverages and has not been corrected for a 0.8 eV charging shift. (b) Attenuation of the integrated C 1s, N 1s, and O 1s signals vs Cu deposition time.
- Figure Four.** Decrease of the Cu 2p_{3/2} intensity following annealing at various temperatures. The insert compares the Cu 2p_{3/2} lineshape before heating (crosses) and after heating to 575 K (squares) and shows that the lineshape is unchanged. Data is from the same sample as Fig. 2 and the binding energy scale has not been corrected for a 4 eV charging shift.



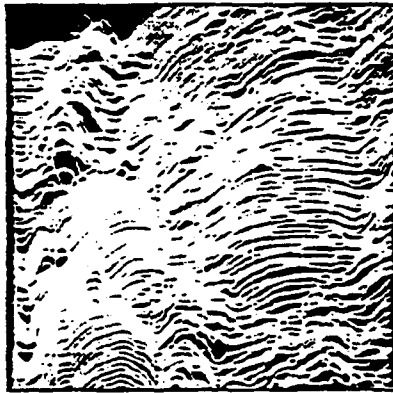
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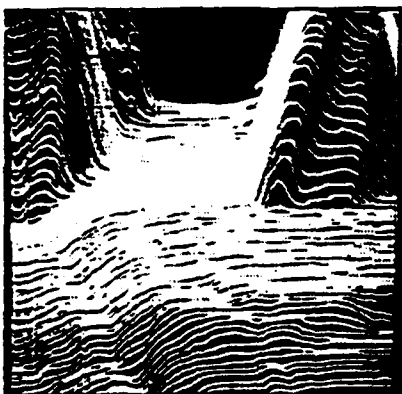
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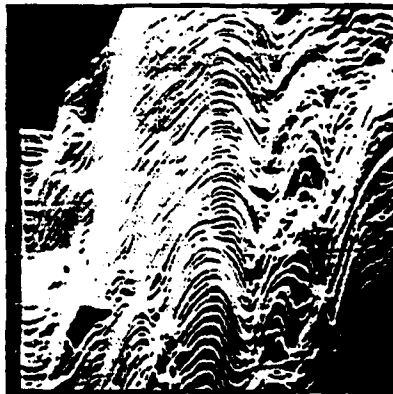
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FIG. 1

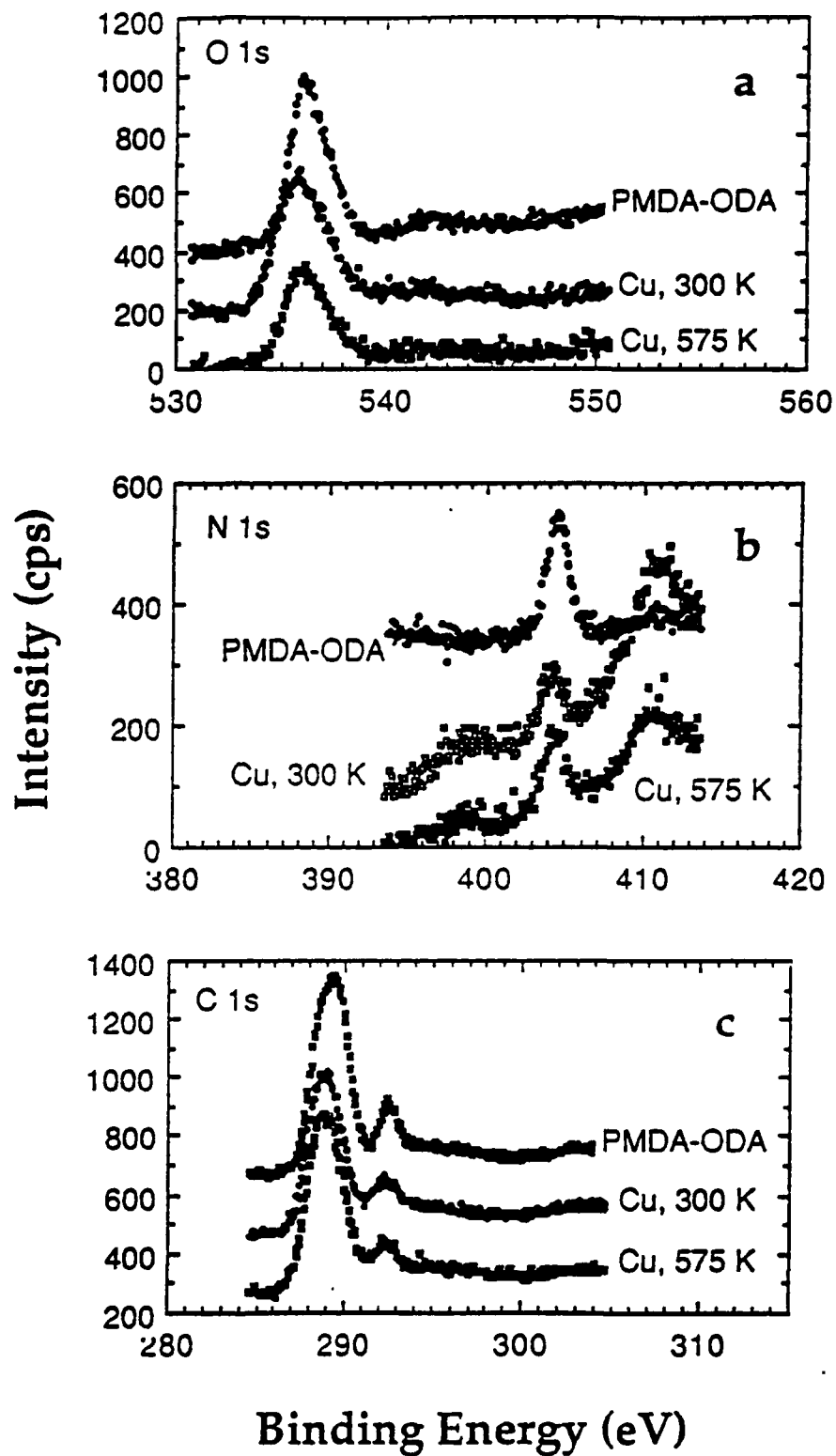


Fig. 2

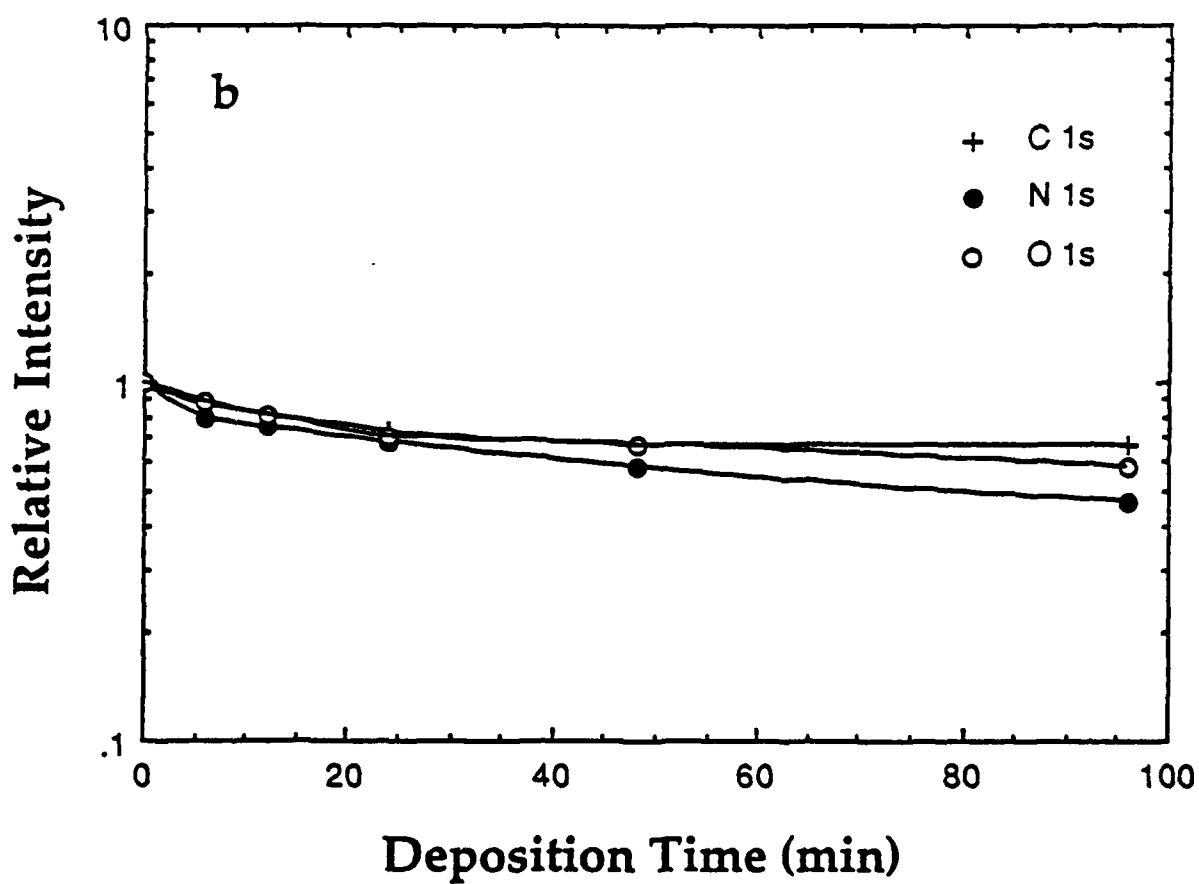
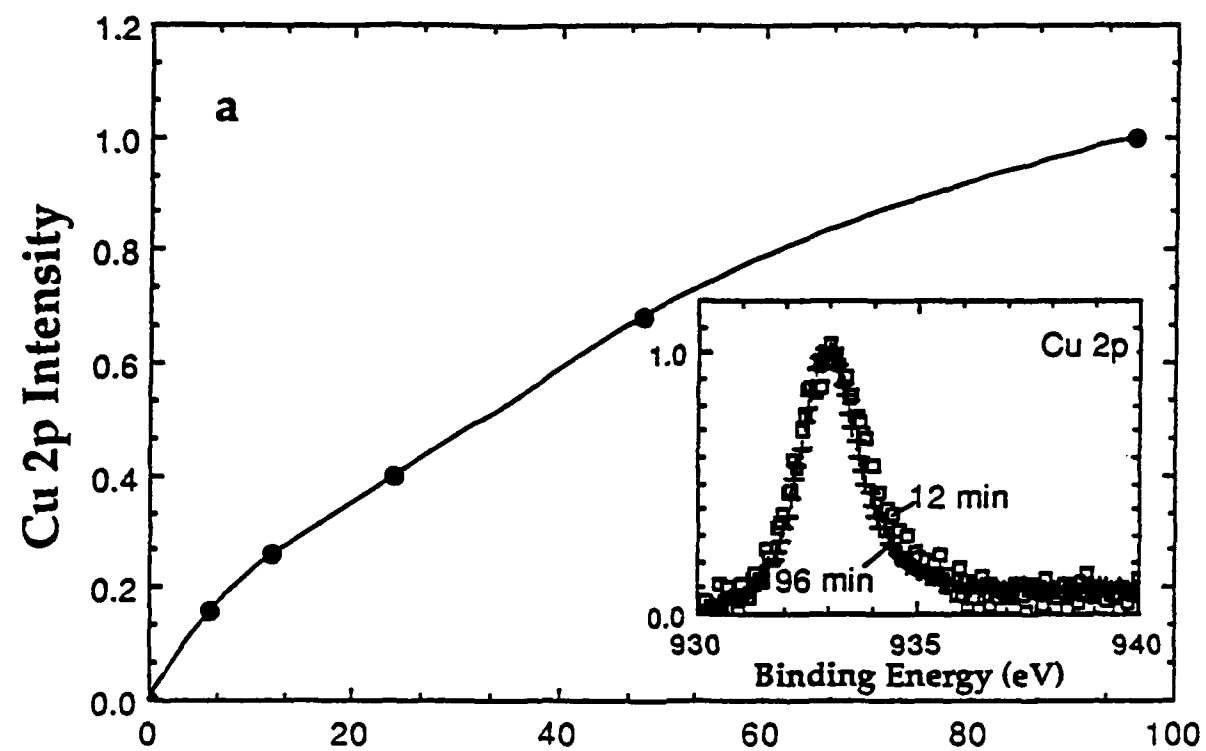


Fig. 3.

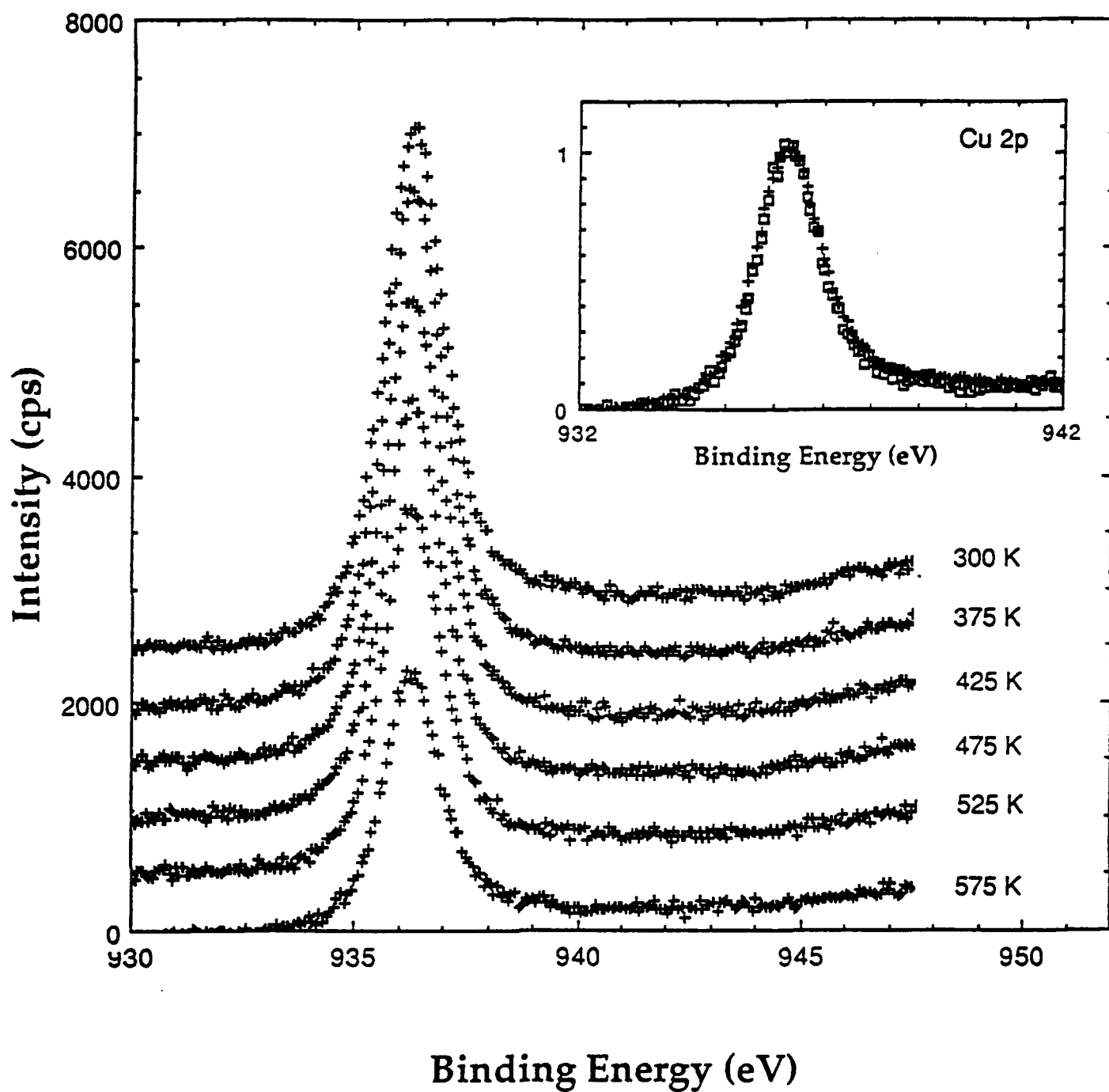


Fig. 4.

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